DENSITY AND MOLAR VOLUME OF MELTS IN THE SYSTEMS LiCl-NaCl, NaCl-RbCl AND NaCl-CsCl

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24 December 1973

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TRANSLATION

In Reply Refer to:
FSTC-HT-23-1340-73
DIA Task No. T70-23-01

Date: 24 December 1973

ENGLISH TITLE: Density and Molar Volume of Melts in the Systems LiCl-NaCl, NaCl-RbCl and NaCl-CsCl

SOURCE: Elektrokhimiya rasplarlennykh solevykh i tverdykh elektrolitov, Trudy Instituta Elektrokhimii, Akademiya Nauk SSSR, Ural'skiy Filial, Issue 16, 1970, pp. 17-20

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LANGUAGE: Russian

COUNTRY: USSR

REQUESTOR: GE-Busi

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ABSTRACT: The densities of molten NaCl-CsCl, NaCl-RbCl and LiCl-NaCl systems were measured by the hydrostatic weighing method over the entire concentration range. The molar volumes and their deviations from additivity at 800 and 850° C were calculated from the experimental data. In all melts, the deviations of molar volumes from the ideal were positive, with the greatest deviations observed in melts containing from 0 to 75% of the cations having the greatest ionic moments. This is evidence that the second coordination sphere plays the principal part in "breaking up" the structures of these melts.

Alkali metal halides are typical ionic fluids. Their structure can be represented as a chaotic mixture of complex MeX_4^{3-} anions and "free" Me^+ cations, the mutual locations of which are disordered and subject to statistical distribution laws. For example, lithium, sodium, rubidium and cesium chlorides are represented symbolically by the formulas $Li_3[LiCl_4]$, $Na_3[NaCl_4]$, $Rb_3[RbCl_4]$ and $Cs_3[CsCl_4]$, respectively. Its polarizing action on the surrounding anions and complexes increases with increase in the ionic moment of the central cation [1].

According to this autocomplex model, in binary solutions, it is precisely the cations having the larger ionic moment which emerge as complex-forming ones, and the cations of the other component are displaced into the second coordination sphere. Strengthening of the bonds takes place in the first coordination sphere, owing to superposition of ion-dipole interactions on ion-ion interactions. At the same time, the bonds in complexes of anions with cations in the second sphere are weakened, as a result of increase in the distance between them. As a consequence of this rearrangement, changes in packing density can be expected. The size of the complex anion $NaCl_4^{3-}$ is less than that of $RbCl_4^{3-}$ and of $CsCl_4^{3-}$, but larger than that of $LiCl_4^{3-}$. Therefore, in the NaCl-RbCl, NaCl-CsCl, and LiCl-NaCl mixtures, the packing of rubidium cations around the $NaCl_4^{3-}$ anions and of sodium around $LiCl_4^{3-}$ should be less dense than the packing of rubidium around $RbCl_4^{3-}$, cesium around $CsCl_4^{3-}$ and sodium around $NaCl_4^{3-}$, respectively.

If this effect exists, it should be manifested in deviations of the molar volumes of binary mixtures from additivity, in which the more sharply the radii of the components of the cation mixture differ, the greater the deviations will be.

There are no experimental data in the literature, by which a judgment could be made as to changes in molar volumes of the molten NaCl-LiCl, NaCl-RbCl, and

NaCl-CsCl mixtures of interest to us. Therefore, the purpose of this work is determination of the densities of the systems referred to above, over the entire range of concentrations, in the 650-800° C temperature range.

The densities were measured by a method which was described in detail in work [2]. Chemically pure grade sodium chloride was used in the investigations. Chemically pure grade cesium and rubidium chlorides were recrystallized repeatedly. Lithium chloride was prepared by the method proposed by Laitinen [3]. The experimental data, processed by the least squares method, gave temperature vs. density equations (Table 1).

TABLE 1: TEMPERATURE VS. DENSITY OF MOLTEN SYSTEMS

a Мол. доля второго компонента	t, °C	b Плотность, $г/см^3$
	LiCl — NaCl	
0	630–800	$d=1,8963-0,0001158\ t\pm0,0005$
0,1	660–850	$d=1,7947-0,0004573\ t\pm0,0015$
0,25	610–850	$d=1,8249-0,0001724\ t\pm0,0020$
0,40	670–860	$d=1,8128-0,0000660\ t\pm0,0010$
0,55	690–850	$d=1,8828-0,0001922\ t\pm0,0003$
0,85	790–860	$d=1,9199-0,0005270\ t\pm0,0003$
1,00	810–910	$d=1,9941-0,0005560\ t\pm0,0003$
	NaCl — RbCl	
0,10	780–860	$d=2,1090-0,0006239\ t\pm0,0003$
0,25	750–860	$d=2,2442-0,0006553\ t\pm0,0003$
0,45	750–850	$d=2,4424-0,0007173\ t\pm0,0003$
0,65	770–850	$d=2,6515-0,0008173\ t\pm0,0003$
0,90	760–850	$d=2,8138-0,0008565\ t\pm0,0010$
1,00	775–850	$d=2,8770-0,0008767\ t\pm0,0003$
	NaCl — CsCl	
0,10	800–895	$d=2,1523-0,0005907\ t\pm0,0003$
0,25	760–860	$d=2,3035-0,0007631\ t\pm0,0007$
0,40	700–860	$d=2,8051-0,0008699\ t\pm0,0010$
0,55	650–850	$d=3,0548-0,0009941\ t\pm0,0003$
0,70	621–870	$d=3,2150-0,0010021\ t\pm0,0009$
0,85	660–870	$d=3,4170-0,0010179\ t\pm0,0010$
1,00	670–900	$d=3,4969-0,0010148\ t\pm0,0005$

Key: a. Mole fraction of second component
b. Density, g/cm^3

[Translator's note: Commas in tabulated figures in this and succeeding tables are equivalent to decimal points.]

Our results on density of the individual sodium and rubidium chlorides satisfactorily match the data of other authors [14]. In plots of the density isotherms of melts of the systems studied from the experimental data (Fig. 1), the greatest positive deviation from additivity is observed for the NaCl-CsCl system and somewhat less for NaCl-RbCl. The density changes additively for the LiCl-NaCl system.

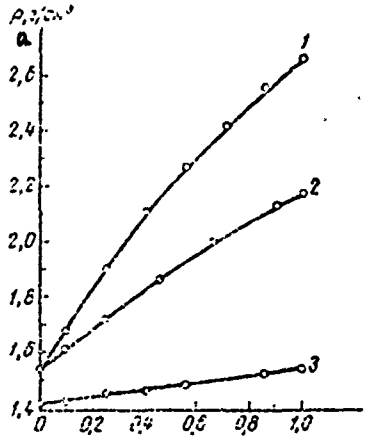

Fig. 1: Density Isotherms of Molten Mixtures at 800° C.

1 - NaCl-CsCl; 2 - NaCl-RbCl; 3 - LiCl-NaCl;

The mole fractions of the second component are plotted on the abscissa.

Key: a. Density ρ, g/cm^3

The molar volumes of all salt mixtures studied and their deviations from additivity, calculated for 800 and 850°, are presented in Table 2.

The relative deviations from additivity of the molar volumes of the mixtures studied at 800°, over the entire concentration range, are positive (fig. 2). The maximum deviations are observed in the region of 75 mole % NaCl, for the NaCl-RbCl and NaCl-CsCl systems, when one sodium cation in the second coordination spheres is replaced by a rubidium and a cesium cation, respectively, and in the 75 mole % LiCl region, for the LiCl-NaCl system, when a lithium cation in the second sphere is replaced by a sodium cation. The numerical values of these deviations increase with increase in difference in the cation radii $\Delta r = r_i - r_j$, where r_i and r_j are the cation radii. For mixtures containing 75-100 mole % RbCl, CsCl and NaCl, when the complexes $RbCl_4^{3-}$, $CsCl_4^{3-}$, and $NaCl_4^{3-}$ are formed, the value of the molar volume differs very insignificantly from the additive values.

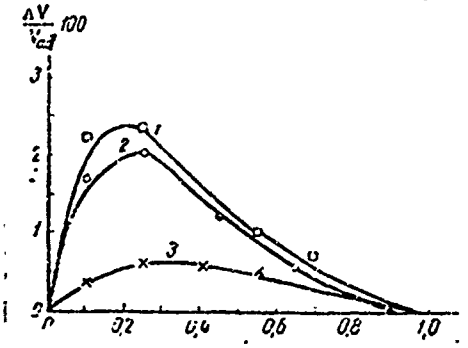

Fig. 2: Deviations from Additivity of Molar Volumes of Molten Mixtures at 800° C:

1 - NaCl-CsCl; 2 - NaCl-RbCl; 3 - LiCl-NaCl;

Mole fractions of the second component are plotted on the abscissa.

TABLE 2: MOLAR VOLUME OF MOLTEN SALT MIXTURES

a Мол. доля второго компонента	b $V_{эксп}$	c $V_{ад}$	ΔV	$\frac{\Delta V}{V}$, %	b $V_{эксп}$	c $V_{ад}$	ΔV	$\frac{\Delta V}{V}$, %
	800°				850°			
LiCl — NaCl								
0	28,89	29,89	0	0	30,36	30,36	0	0
0,10	30,79	30,67	0,12	0,39	31,30	31,15	0,14	0,45
0,25	32,06	31,86	0,20	0,63	32,60	32,37	0,23	0,71
0,40	33,21	33,02	0,19	0,57	33,74	33,58	0,16	0,49
0,55	34,39	34,20	0,19	0,55	34,98	34,78	0,20	0,57
0,85	36,65	36,55	0,10	0,28	37,30	37,19	0,11	0,30
1,00	37,72	37,72	0	0	38,41	38,41	0	0
NaCl — RbCl								
0	37,72	37,72	0	0	38,41	38,41	0	0
0,10	40,18	39,50	0,68	1,72	40,98	40,24	0,74	1,84
0,25	43,06	42,19	0,87	2,07	43,90	42,99	0,91	2,12
0,45	46,32	45,76	0,56	1,23	47,23	46,65	0,58	1,24
0,65	49,61	49,33	0,31	0,63	50,63	50,30	0,33	0,60
0,90	53,88	53,79	0,09	0,02	54,98	54,88	0,10	0,02
1,00	55,74	55,74	0	0	56,72	56,72	0	0
NaCl — CsCl								
0	37,72	37,72	0	0	38,41	38,41	0	0
0,10	41,32	40,29	1,03	2,55	42,07	41,03	1,01	2,50
0,25	45,32	44,13	1,19	2,70	46,25	44,96	1,29	2,87
0,40	48,52	47,98	0,54	1,12	49,54	48,90	0,64	1,31
0,55	52,39	51,83	0,56	1,08	53,56	52,84	0,72	1,36
0,70	56,10	55,68	0,42	0,75	57,29	56,77	0,52	0,91
0,85	59,41	59,52	0,11	—0,17	60,62	60,70	—0,08	—0,13
1,00	63,37	63,37	0	0	64,64	64,64	0	0

Key: a. **Mole fraction of second component**

b. V_{exp}

c. V_{ad}

Thus, the positive deviations of the molar volumes which we observed are connected mainly with rearrangement of the second coordination sphere.

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